# Chemistry

## Lecture 11

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## Atomic Structure

**Outline:**

- Concept of orbital
- Electronic configuration
- Discovery and properties of proton (positive rays)
- Quantum numbers
- Shapes of orbitals

### Atomic Structure

**Atom:** Smallest particle of an element that can take part in chemical reaction

**Nucleus:** Centre of an atom where mass of whole atom is concentrated

**Nucleons (Neutron + Proton):** Particles inside nucleus

**Electrons ($e^-$): ($_{-1}^{0}e$)** Particles outside the nucleus, revolving in orbitals

| Anode (Canal) Rays [Positive Rays] |
|---|
| In discharge tube (discovered by Crooks)<br>Positive rays were discovered by Goldstein |
| Pressure kept low but at 0.01 torr, the glow disappears |
| Voltage = 5000-10000 volts<br>Voltage applied depends on: i. Length of glass tube ii. Pressure in glass tube |
| Produced by ionization of gas $M \rightarrow M^{+1} + 1e^-$ |
| Passing through the magnetic field, gets deflected (show they are charged) |
| In electric field, gets deflected toward negative plate (show positively charged) |
| Passes through canals of cathode, so called canal rays |
| Produce flashes on ZnS plate |
| Called positive rays due to carrying positive charge |
| Possess momentum |
| Seems like coming from side of anode, so called anode rays |
| The mass of +ve particle is never less than that of a proton |
| Mass of electron 1836 less than proton |
| e/m value depends on nature of residual gas. Heavier the gas smaller will be the e/m value of gas |
| e/m value less than electron (1836 times in case of proton) |
| Maximum e/m is for $H_2$ gas (is proton) |
| Rutherford suggested name proton |

## Distribution of Masses and Charges

| Sub-atomic Particle | symbol | Charge (Coulombs) | Relative Charge | Mass (kg) | Mass (amu) | Relative mass |
|---|---|---|---|---|---|---|
| Proton | $P^+$ | $+1.602 \times 10^{-19}$ | +1 | $1.6726 \times 10^{-27}$ | 1.0073 | 1 |
| Neutron | n | 0 | 0 | $1.6750 \times 10^{-27}$ | 1.0087 | 1 |
| Electron | $e^-$ | $-1.602 \times 10^{-19}$ | -1 | $9.1095 \times 10^{-31}$ | $5.4858 \times 10^{-4}$ | $\frac{1}{1836}$ of proton |

**1 amu = $1.661 \times 10^{-27}$ kg**

## Quantum Numbers (position of electron)

Gives acceptable solution of Schrödinger equation

Information

i. Period number

ii. Group number

iii. Valency (related to valence electrons)

No. of shells = period number

Electrons in valence shell = Group number

| Principal (n) | Azimuthal ($\ell$) | Magnetic (m) | Spin (s) |
|---|---|---|---|
| Gives no. of shells (n=1,2,3…) | Gives number of subshells in shell ($\ell$=0,1,2,3….(n- $\ell$))<br>Explains fine line structure<br>Gives shape of orbitals<br>No. of subshells = principal quantum number (n) | Atomic orbitals<br>Explains Zeeman's effect | Explain doublet line structure of in the spectrum of metals |
| n=1 → K-Shell, n=2 → L-Shell, n=3 → M-Shell, n=4 → N-Shell etc | $\ell$=0(s)[sharp], $\ell$ =1(p)[principal], $\ell$=2 (d)[diffused], $\ell$ = 3 (f)[fundamental] | Orientation of atomic orbitals in magnetic field | Explains the spin of electron |
| n is positive whole number integer | s(spherical), p(dumbbell)<br>d(double dumbbell or sausage), f(complicated) | Values of "m" given by<br>$2\ell + 1$<br>m = 0, ±1, ±2, ±3…… | While revolving around nucleus, electron spins around its own axis |
| Gives atomic radius (distance of electron from nucleus) as<br>$r = 0.529\ ^oA \times n^2$<br>'r' increases with 'n' | ≫ **n=1** → $\ell$ = 0 s 1s<br>≫ **n=2** → $\ell$ = 0 s 2s<br>$\ell$ = 1 p 2p<br>≫ **n=3** → $\ell$ = 0 s 3s<br>$\ell$ = 1 p 3p<br>$\ell$ = 2 d 3d<br>≫ **n=4** → $\ell$ = 0 s 4s<br>$\ell$ = 1 p 4p<br>$\ell$ = 2 d 4d | Each orbital has only **2 es**$^{-1}$<br>Atomic orbitals of a subshell are degenerate | Spin clockwise or anti-clockwise (+1/2, -1/2) 50% chances of each |
| Gives energy as<br>$E = \frac{-1313.315}{n^2}$ kjmol$^{-1}$ | | ≫ **$\ell$ = 0** → s → m = 0 (only one orientation)<br>≫ **$\ell$ = 1** → p → m = 0, ±1 (3 orientations i.e. $p_x$, $p_y$ $p_z$)<br>≫ **$\ell$ = 2** → d → m = 0, ±1, | |

| | | | |
|---|---|---|---|
| 'E' increases with 'n' | $\ell = 3$ f 4f | $\pm 2$ (5 orientations i.e. $d_{xy}$, $d_{yz}$, $d_{zx}$, $d_{x^2-y^2}$, $d_{z^2}$) | |
| No. of electrons in shell given by $2n^2$ | No. of electrons in a subshell given by $2(2\ell + 1)$ | $\gg \ell = 3 \rightarrow$ f $\rightarrow$ m = 0, $\pm 1$, $\pm 2$, $\pm 3$ (7 orientations) | |
| | s = 2, p = 6, d = 10, f = 14 | Atomic orbitals in shell ($n^2$) | ---------- |

## Concept of Orbital

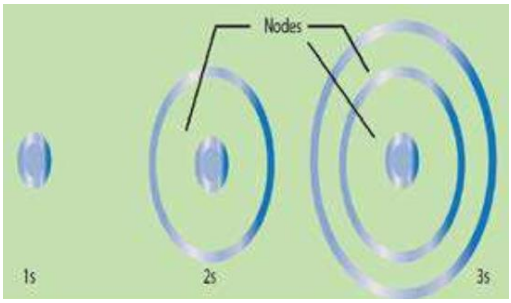
- ✓ It is three dimensional space around nucleus where the probability of finding electron is maximum i.e. 95 %
- ✓ Orbitals have different shapes e.g. s-orbital has spherical, p-orbitals have dumb-bell shapes
- ✓ All orbitals have directional character except s-orbital
- ✓ It represents three dimensional motion of electron
- ✓ An orbital can have maximum of 2 electrons

## Shapes of Orbitals (3 dimensional)

- s > p > d > f (penetration effect) s < p < d < f (relative energy)

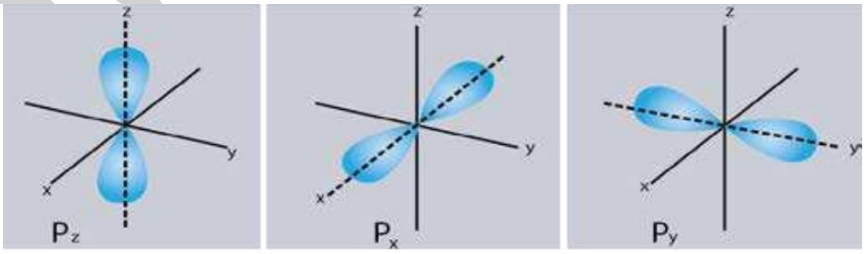
**Shape of s:**

- ❖ Spherical
- ❖ Size and energy of s-orbital increases with increase in value of "n" i.e. 3s > 2s > 1s
- ❖ The probability for finding the electron is zero between two orbitals. This place is called nodal plane or nodal surface




**Shape of p:**

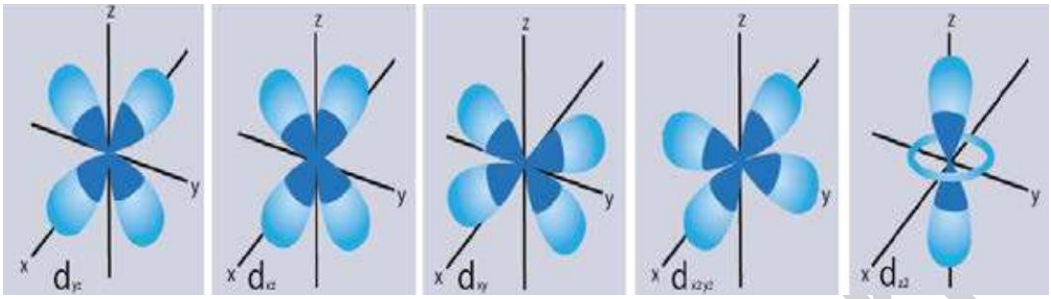
- ❖ Dumb-bell (two lobes)
- ❖ Size and energy of p-orbital increases with increase in value of "n" i.e. 3p > 2p
- ❖ Three atomic orbitals [$p_x$(along x-axis), $p_y$ (along y-axis), $p_z$ (along z-axis)] are degenerate (same energy)




**Shape of d:**

- ❖ Double dumb-bell (four lobes)
- ❖ Size and energy of d-orbital increases with increase in value of "n" i.e. 4d > 3d

- Five atomic orbitals [$d_{xy}$ , $d_{yz}$ , $d_{zx}$ (these 3 are between the axis), $d_{x2-y2}$ , $d_{z2}$ (both are the on axis)] are degenerate (same energy)




## Electronic Configuration

- Distribution of electrons in subshells/atomic orbitals
- **(n + $\ell$) Rule:**
  - Used for arranging subshells
  - Subshells are arranged in the increasing order of (n + $\ell$) values and if any two subshells have the same (n + $\ell$) values, then that subshell is placed first whose "n" value is smaller
  - 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s and so no
- **Aufbau Principle:**
  - The electrons should be filled in energy subshells in order of increasing energy values The electrons are first placed in 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s and so on
- **Pauli's Exclusion Principle:**
  - It is impossible for two electrons residing in the same orbital of a poly-electron atom to have the same values of four quantum numbers

    OR
  - Two electrons in the same orbital should have opposite spins (↓↑ )
- **Hund's Rule:**
  - Tells about valency (by no. of unpaired electrons)
  - If degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins

While writing electronic configuration;

- $d^4$ and $d^9$ are not stable, so they get 1 electron from nearby s-subshell to become $d^5$, $d^{10}$ respectively

## Planck's Quantum theory

- Energy is not emitted or absorbed continuously. Rather, it is emitted or absorbed in a discontinuous manner and in the form of wave packets called quanta. Each wave packet or quantum is associated with a definite amount of energy
- In case of light, the quantum of energy is often called photon.
- The amount of energy associated with a quantum of radiation is proportional to the frequency ($\upsilon$) of the radiation.

  **Frequency** is the number of waves passing through a point per second. Its units are hertz, cycles/sec.

  $$\mathbf{E} \propto \boldsymbol{\upsilon}$$

  $$\mathbf{E = h\,\upsilon \ldots\ldots\ldots 1}$$

  Where 'h' is a constant known as Planck's constant and its value is $6.626 \times 10^{-34}$ Js. It is, in fact, the ratio of energy and the frequency of a photon.
- A body can emit or absorb energy only in terms of quanta.

  $$\mathbf{E = h\,\upsilon \ldots\ldots\ldots 1}$$

  The frequency 'ν' is related to the wavelength of the photon as;

  $$\boldsymbol{\upsilon = c/\lambda}$$ put in Eq. 1
- Greater the wavelength, smaller the frequency of photon.

  $$\mathbf{E = hc/\lambda \ldots\ldots\ldots 2}$$

  **Wavelength** is the distance between the two adjacent crests or troughs and expressed in Å, nm, pm. ($1Å = 10^{-10}$ m, $1nm = 10^{-9}$ m, $1pm = 10^{-12}$ m)
- Greater the wavelength associated with the photon, smaller is its energy.

  **Wave number (ν)** is the number of waves per unit length, and is reciprocal to wavelength. Units are $cm^{-1}$, $m^{-1}$.

  $$\bar{\upsilon} = \mathbf{1/\lambda}$$

  Putting this value equation (2)

  $$\mathbf{E = hc}\,\bar{\upsilon}$$

  So, the energy of a photon is related to frequency, wavelength and wave number
- Greater the wave number of photons, greater is the energy associated with them
- Speed/velocity (c) is distance through which a particular wave travels in one second

  Measured in $ms^{-1}$, the velocity of light in vacuum is $3 \times 10^{8}$ $ms^{-1}$